

# Renormalization of Optical Excitations in Molecules near a Metal Surface

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(Dated: January 13, 2013)

The lowest electronic excitations of benzene and a set of donor-acceptor molecular complexes are calculated for the gas phase and on the Al(111) surface using the many-body Bethe-Salpeter equation (BSE). The energy of the charge-transfer excitations obtained for the gas phase complexes are found to be around 10% lower than the experimental values. When the molecules are placed outside the surface, the enhanced screening from the metal reduces the exciton binding energies by several eVs and the transition energies by up to 1 eV depending on the size of the transition-generated dipole. As a striking consequence we find that close to the metal surface the optical gap of benzene can exceed its quasiparticle gap. A classical image charge model for the screened Coulomb interaction can account for all these effects which, on the other hand, are completely missed by standard time-dependent density functional theory.

PACS numbers: 78.67.-n, 73.20.-r, 82.37.Vb, 85.65.+h

The performance of organic-based (opto-)electronics devices such as organic and dye sensitized solar cells, organic transistors and light emitting diodes[1–3], depends crucially on the interface between the “active” organic region and the metallic or semiconducting electrodes. In particular, the position of the molecular energy levels relative to the metal Fermi level, and the size of the electron-hole binding energy are of key importance for the charge transport across an organic-metal interface and for the dissociation of photoexcited excitons at a donor-acceptor interface. The purpose of this Letter is to illustrate how the excitation spectrum of a molecule is affected by the presence of a nearby metal surface, see Fig. 1.

Elementary excitations of many-electron systems consist two basic types: (i) Quasiparticle (QP) excitations which involve the addition or removal of an electron from the system, and (ii) optical excitations which involve the promotion of an electron from one electronic level to another. In the case of molecules on metal surfaces the former type can be probed in transport- or photoemission experiments[4, 5] while the latter can be probed by electron energy loss- or surface-enhanced Raman spectroscopy[6–8]. It has recently been demonstrated both experimentally[4, 9] and on the basis of many-body calculations[10–12], that when a molecule is adsorbed on a polarizable substrate its QP gap, i.e. the difference between ionization potential ( $I_p$ ) and electron affinity ( $E_a$ ), is reduced as a result of image charge interactions. The same mechanism was shown earlier to lead to a narrowing of the band gap at semiconductor-metal interfaces[13]. In contrast, similar effects on the optical excitations of adsorbed molecules have so far only been discussed on the basis of phenomenological models[14–16].

An efficient method for the calculation of optical excitations in molecules is the time-dependent density functional theory (TDDFT)[17]. The widely used adiabatic

local density approximation (ALDA) has been quite successful for intramolecular transitions whereas charge-transfer excitations are significantly underestimated.[18] Alternatively, optical excitations can be obtained from the Bethe-Salpeter equation (BSE) which is rooted in many-body perturbation theory[19]. This approach has been successfully used to describe the optical properties of a broad variety of systems including organic and inorganic semiconductors as well as gas-phase molecules[19, 20]. However, applications of the BSE to charge-transfer complexes or metal-molecule interfaces have so far not been reported.

In the first part of this Letter we assess the performance of the BSE approach for describing charge-transfer excitations in a set of four donor-TCNE (tetracyanoethylene) molecular complexes. In the second and main part we investigate how the optical properties of a molecule (here represented by benzene and a benzene-TCNE dimer) change when placed outside an Al(111) surface.

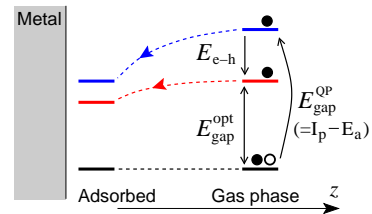


FIG. 1: (Color online) Schematic illustration of the narrowing of the energy gaps of a molecule as it approaches a metal surface. The reduction of the QP gap is due to the interaction of the added electron/hole with its image charge in the metal. Similarly the optical gap is reduced due to the interaction of the transition dipole with its induced image dipole. Finally, the exciton binding energy ( $E_{e-h}$ ) is also reduced because the electron-hole interaction is screened by the metal.

TABLE I: Experimental and calculated energy gaps of the four donor-TCNE complexes in the gas phase. The experimental (calculated) QP gaps have been obtained as the difference between the ionization potential of the free donor (the HOMO level) and electron affinity of free TCNE (the LUMO level). The optical gap is the corresponding  $\pi(\text{donor}) \rightarrow \pi^*(\text{TCNE})$  singlet transition of the complex.

Donor	$E_{\text{gap}}^{\text{QP}}$ (eV)			$E_{\text{gap}}^{\text{opt}}$ (eV)				$E_{\text{e-h}}$ (eV)		
	G <sub>0</sub> W <sub>0</sub>	$\Delta\text{SCF}$	<sup>a</sup> Exp.	BSE	TDLDA	$\Delta\text{SCF}$	<sup>b</sup> Exp.	G <sub>0</sub> W <sub>0</sub> -BSE	$\Delta\text{SCF}$	<sup>a,b</sup> Exp.
Benzene	6.31	6.07	6.33	3.22	1.47	3.49	3.59	-3.09	-2.58	-2.74
Toluene	5.81	5.50	5.92	2.82	1.28	2.87	3.36	-2.99	-2.63	-2.56
O-xylene	5.59	5.21	5.65	2.73	1.42	2.57	3.15	-2.87	-2.64	-2.50
Naphthalene	5.04	4.68	5.23	2.38	1.93	2.12	2.60	-2.66	-2.56	-2.63
MAE	0.11	0.42	0.0	0.39	1.65	0.42	0.0	0.30	0.11	0.0

<sup>a</sup>Ionization potentials from Refs. 24, 25. Electron affinity of TCNE from Refs. 26, 27 (we used the value 2.91 eV).

<sup>b</sup>From Ref. 28

The gas-phase calculations were performed in a 15 Å cubic supercell with the donor-TCNE dimers fixed in the structures reported in Ref. 21. The donor-TCNE distance ( $d$ ) lie in the range 3.57 – 3.91 Å for the four complexes. For the metal-molecule interfaces we used a supercell containing three layers of Al(111) with  $5 \times 5$  atoms in each layer. The molecules in their gas-phase structure were placed a distance  $z$  above the surface followed by 13 Å of vacuum. DFT-LDA calculations were performed with the PWSCF code[22] using a 40 Hartree plane-wave cut-off and a  $2 \times 2 \times 1$   $k$ -point mesh (only the  $\Gamma$ -point was used for the gas-phase calculations). G<sub>0</sub>W<sub>0</sub> and BSE calculations were performed with the Yambo code[23] using the LDA wave functions and eigenvalues as input and a plasmon pole model fitted to the dielectric matrix at imaginary frequencies 0 and 1 Hartree. For the dielectric matrix we used a 30 eV cut-off for the sum over virtual states. We have verified that increasing the number of  $k$ -points in the surface plane to from  $2 \times 2$  to  $4 \times 4$  changes the G<sub>0</sub>W<sub>0</sub> and BSE energies by less than 0.05 eV. The G<sub>0</sub>W<sub>0</sub> and BSE supercell calculations for the isolated molecules have been performed with a truncated Coulomb interaction in order to avoid spurious interactions between the repeated images.

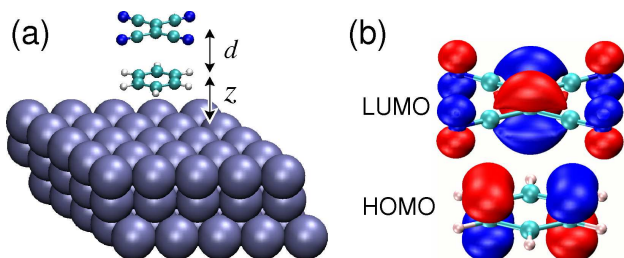


FIG. 2: (Color online) (a) Supercell used to describe the benzene and benzene-TCNE molecules on Al(111). (b) Contour plots of the HOMO and LUMO orbitals of the benzene-TCNE charge transfer complex.

Table I summarizes our results for the four different donor-TCNE complexes in the gas-phase. The three columns show the calculated and experimental QP gaps, optical gaps, and electron-hole interactions. The latter has been defined according to [29]

$$E_{\text{gap}}^{\text{opt}} = E_{\text{gap}}^{\text{QP}} + E_{\text{e-h}} \quad (1)$$

In addition to the many-body results we have performed TDLDA and  $\Delta\text{SCF}(\text{LDA})$  calculations for comparison. The results obtained with the two latter methods are in good agreement with another recent study[30].

Both BSE and  $\Delta\text{SCF}$  significantly improve the charge-transfer excitations compared to TDLDA – in particular the ordering of the gap sizes becomes correct. The error in the BSE optical gap is due to the additive effects of an underestimation of the QP gap and overestimation of the  $e$ - $h$  interaction with the latter being the largest effect. In contrast, the  $\Delta\text{SCF}$  method provides an accurate description of the  $e$ - $h$  interaction, while the underestimation of the QP gap is the main source of error. We mention that recent TDDFT calculations employing a range-separated functional achieved a mean absolute error (MAE) of only 0.12 eV for the four molecules by tuning the range parameter separately for each molecule[21]. A recently introduced constrained variational DFT scheme yields a MAE of around 0.2 eV.[30]

We next consider how the excitation energies are affected when the molecules are placed next to a metal surface. Here we focus on the regime where hybridization between the metal and molecule wave functions can be neglected; we have found this to be the case for  $z \geq 4.0$  Å. In this regime the COHSEX approximation to the GW self-energy can be used to obtain the change in the QP energy levels[10]

$$\Delta E_n^{\text{QP}} = \pm \frac{1}{2} (\psi_n^* \psi_n | \Delta W | \psi_n^* \psi_n) \quad (2)$$

where the sign is positive (negative) for empty (occupied)

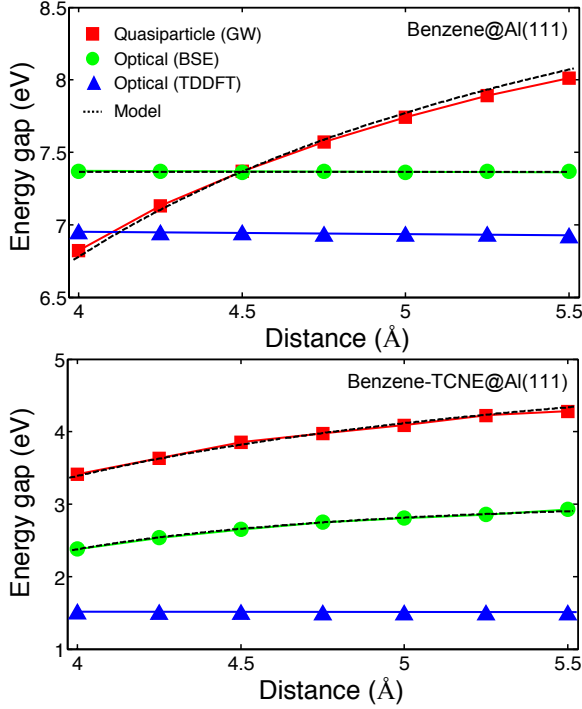


FIG. 3: (Color online) Calculated QP and optical gaps of benzene (upper panel) and benzene-TCNE (lower panel) as a function of distance to the Al(111) surface.

states and we have introduced the shorthand

$$(f|A|g) = \int \int f(r)A(r,r')g(r')drdr'. \quad (3)$$

The change in the QP gap thus becomes

$$\Delta E_{\text{gap}}^{\text{QP}} = \frac{1}{2}[(\psi_H^* \psi_H | \Delta W | \psi_H^* \psi_H) + (\psi_L^* \psi_L | \Delta W | \psi_L^* \psi_L)] \quad (4)$$

The potential  $\Delta W \equiv W_{\text{mol@surf}} - W_{\text{mol}}$ , is the change in the (static) screened Coulomb interaction due to the presence of the surface. Physically it represents the electrostatic potential at point  $r'$  due to the polarization of the metal induced by a point charge at point  $r$ . Clearly this interaction is attractive, i.e.  $\Delta W < 0$ . The simplest approximation to  $\Delta W$  is the classical image potential model

$$\Delta W(r, r') = -\frac{1}{2}[(x' - x)^2 + (y' - y)^2 + (z' + z)^2]^{-1/2} \quad (5)$$

which reduces to the well known form  $1/4z$  for  $r = r'$ .

In Fig. 3 (red squares) we show the calculated QP gap of benzene (upper panel) and benzene-TCNE (lower panel) as a function of the distance to the Al(111) surface. The GW results show the expected closing of the gap due to the image charge effect[10–12]. The dashed lines show the result of the classical image charge model Eq. (5)

where the HOMO and LUMO charge distributions have been approximated by point charges and the image plane position has been used as fitting parameter[12].

Within the standard BSE approach, the optical excitations are obtained by diagonalizing an effective two-particle Hamiltonian within a space of single-particle transitions[19]. To simplify the discussion we shall assume that we can neglect the mixing of single-particle transitions (this in fact turns out to be a valid approximation). In this case the  $e$ - $h$  interaction corresponding to the HOMO-LUMO transition is simply given by the diagonal element of the exchange-correlation kernel

$$E_{e-h} = (\psi_H^* \psi_L | v | \psi_L^* \psi_H) - (\psi_H^* \psi_H | W | \psi_L^* \psi_L) \quad (6)$$

The first term is a repulsive electron-hole exchange interaction and the second term is a direct screened Coulomb interaction. The change in the  $e$ - $h$  interaction due to the metal surface is then

$$\Delta E_{e-h} = -(\psi_H^* \psi_H | \Delta W | \psi_L^* \psi_L) \quad (7)$$

(where we have assumed weak coupling so that the orbitals of the adsorbed molecule are similar to those in the gas phase.) Combining Eqs. (1), (4), and (7) we arrive at the following expression for the change in the optical gap

$$\Delta E_{\text{gap}}^{\text{opt}} = \frac{1}{2}(\psi_H^* \psi_H - \psi_L^* \psi_L | \Delta W | \psi_H^* \psi_H - \psi_L^* \psi_L) \quad (8)$$

This form is very suggestive showing that the change in optical gap is given by the transition-generated dipole interacting with its image in the metal surface. Since  $\Delta W < 0$  the optical gap is always reduced upon adsorption. We stress that the static COHSEX and “diagonal exciton” approximations have been used in the discussion above for illustrative purposes only, and they have not been applied in the *ab-initio* calculations.

In Fig. 3 we show the optical gap of the molecules calculated from the BSE (green circles) and ALDA (blue triangles). The optical gaps correspond to the  $\pi \rightarrow \pi^*$  charge-transfer excitation of benzene-TCNE and the  $^1A_{1g} \rightarrow ^1E_{1u}$  transition in benzene which is the brightest of the four HOMO-LUMO transitions. Focusing first on benzene (upper panel) both calculations yield no change in the optical gap upon adsorption. This is easily understood from Eq. (8) since the dipole moment of the HOMO-LUMO transition in benzene is negligible. Another way of stating this is that the change in the QP gap is completely outbalanced by the weakening of the  $e$ - $h$  interaction due to screening. This is in good agreement with experiments on benzene adsorbed on the Ag(111) surface which showed a change in the optical gap of less than 0.05 eV as compared to benzene in the gas-phase[6].

Interestingly, for distances  $z < 4.5$  Å, the QP gap is smaller than the optical gap implying, somewhat counter-intuitively, that the electron-hole interaction is repulsive.

According to Eq. (6) this can occur if the screened direct  $e$ - $h$  interaction becomes smaller (in absolute value) than the  $e$ - $h$  exchange energy. From a gas-phase calculation we have found that the exchange and screened direct  $e$ - $h$  interactions are 2.0 eV and -5.1 eV, respectively. While the former is unchanged by the metal, the latter is reduced due to the image charge effect. Using the fact that  $|\psi_H(r)|$  and  $|\psi_L(r)|$  are very similar for benzene, Eqs. (4) and (7) show that  $\Delta E_{e-h}$  and  $\Delta E_{gap}^{QP}$  coincide. Since the QP gap of benzene is 10.5 eV in the gas phase, we see from Fig. 3 that  $\Delta E_{gap}^{QP} = 3.1$  eV at  $z = 4.5$  Å. Thus the exchange and screened direct interactions exactly cancel at this distance. At even smaller distances, the exchange dominates the screened direct interaction and the optical gap exceeds the QP gap.

We should stress that the results presented above refer to optical transitions on a single molecule. Since our calculations are performed with periodic boundary conditions we are in fact simulating an infinite array of molecules. Because of the large inter-molecular distance of  $> 10$  Å there is no hybridization between the repeated images. Formally, however, the optical gap of the periodic array is always lower than the QP gap since the electron and hole can be created infinitely far apart in which case the  $e$ - $h$  interaction vanishes. Such excitonic states with the electron and hole located on separate molecules also appear as solutions to the BSE. However, their dipole strength vanishes and they are thus irrelevant for the low coverage of molecules considered here.

For the benzene-TCNE complex the BSE calculation predicts a reduction of the optical gap from its gas-phase value of 3.22 eV to 2.38 eV when the molecule is adsorbed  $z = 4.0$  Å above the metal surface. The change in the optical gap is very accurately reproduced by an image dipole model (dashed line) in which  $\Delta W$  is again modeled by a classical image potential and the HOMO and LUMO charge distributions are modeled as point charges separated by  $d = 3.6$  Å. The classical theory of dipole radiation was used several decades ago to study the related problem of frequency shifts in electric dipole emitters by a nearby metal surface[14–16]. In these studies the role of the frequency dependence of the metal dielectric function has been emphasized. On the other hand, recent GW calculations have shown that the renormalization of the QP levels is well described by the static response function of the metal[10, 11]. On this basis it is reasonable to expect that the use of the static part of  $W$  for the  $e$ - $h$  interaction in the BSE is also a valid approximation.

In summary, we have shown that non-local correlation effects (image charge effects) reduce the optical excitation energies of a molecule by an amount proportional to the transition-generated dipole when it is placed near a polarizable medium. Moreover, electron-hole binding energies can be reduced by several electron volts and, as a consequence, the optical gap of a molecule can exceed its quasiparticle gap close to a metal surface.

The authors thank Tom Ziegler and Angel Rubio for inspiring discussions. We acknowledge support from The Lundbeck Foundation's Center for Atomic-scale Materials Design and the Danish Center for Scientific Computing.

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